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Dragan Mihailovic<sup>a</sup>, Ales Mrzel<sup>a</sup>, Ales Omerzu<sup>a</sup>, Polona Umek<sup>a</sup>, Zvonko Jaglicic<sup>b</sup> & Zvonko Trontelj<sup>b</sup>

<sup>a</sup> Jozef Stefan Institute, Jamova 39, 1000, Ljubljana, Slovenia

<sup>b</sup> Inst. of Mathematics, Physics and Mechanics and Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, Ljubljana, Slovenia

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## Ferromagnetism below 19 K Due to Unpaired Spins on Fullerene Molecules

DRAGAN MIHAJLOVIC<sup>a</sup>, ALES MRZEL<sup>a</sup>, ALES OMERZU<sup>a</sup>,  
POLONA UMEK<sup>a</sup>, ZVONKO JAGLICIC<sup>b</sup> and ZVONKO TRONTELJ<sup>b</sup>

<sup>a</sup>*Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia and* <sup>b</sup>*Inst. of Mathematics, Physics and Mechanics and Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, Ljubljana, Slovenia*

We report on synthesis and physical properties of a fullerene (3-aminophenyl)-1H-1,2-methano-[60]-fullerene-cobaltocene, a molecular organic ferromagnet, with a Curie temperature of 19 K. Near-infrared, mid-infrared and electron spin resonance spectra show that spins reside entirely on the fullerene units from which we deduce that the ferromagnetism is a consequence of the ordering of spins solely on the fullerene units. The ferromagnetic state of the compound is characterized by a low saturation field of 40 oersted and a hysteresis of less than 1 oersted.

**Keywords:** molecular magnetism; susceptibility; fullerenes; ferromagnetism

### INTRODUCTION

The discovery of a new organic material, with clear indications of ferromagnetism at low temperature, namely tetrakis(dimethylamino)ethylene-C<sub>60</sub> (TDAE-C<sub>60</sub>)<sup>[1]</sup> in 1991 raised hopes that FM compounds based on fullerenes with higher T<sub>c</sub>s would soon follow. However, in spite of intensive search for new fullerene based compounds by many groups using different donors (D) and fullerene acceptors (A)<sup>[2]</sup>, TDAE-C<sub>60</sub> has hitherto remained

unique, with its Curie temperature of  $T_c = 16.1\text{K}$  remaining up till now also the highest for any purely organic system. Consequently, subsequent research in the field was mainly devoted to the elucidation of its complex magnetic and electronic properties and seven years since its discovery, the existence of ferromagnetism is still being debated<sup>[3,4,6-9]</sup>, with the most recent experiments on high-quality single crystals apparently confirming the original claims that TDAE-C<sub>60</sub> is a ferromagnet<sup>[10]</sup>, albeit possibly with a reentrant low-temperature spin-glass phase<sup>[11]</sup>. However, the apparent uniqueness of this compound strongly suggested that the spin on the TDAE<sup>+</sup> donor molecule is essential for ferromagnetic ordering, so that synthesis of other new ferromagnetic fullerene compound would be very unlikely. In the mean time, focus has shifted to other materials, and two other non-fullerene based organic ferromagnets have been discovered since<sup>[12-14]</sup>, and a new organic canted antiferromagnet (CAFM) was reported recently<sup>[15]</sup> based on a dithiadiazolyl radical p-NC<sub>6</sub>F<sub>4</sub>CN<sup>•</sup>SSN\* which, although not a proper ferromagnet, showed spontaneous spin canting and ordering below 35.5K.

In this paper we report on the synthesis of a new material exhibiting clear evidence of ferromagnetism below a Curie temperature of  $T_c = 19\text{ K}$ . The compound is a charge transfer complex, (3-aminophenyl)-1H-1,2-methano-[60]-fullerene cobaltocene (APhF-Co) and is composed of a fullerene derivative molecular acceptor and a metallocene donor dicyclopentadienyl-cobalt (Cp<sub>2</sub>Co or cobaltocene).

Regarding the acceptor, among various method for functionalization of C<sub>60</sub> which yield well characterised monoadducts, the cycloaddition of diazo compounds producing methanofullerene is one of the simplest<sup>[16]</sup>. The electronic properties of methanofullerene including (3-aminophenyl)-1H-1,2-methano-[60]-fullerene were found to be similar to parent molecule and

acceptor properties are retained which is an important requirement for doping and formation of charge transfer complexes<sup>[16]</sup>.

The donor molecule cobaltocene is unusual because it has no spin in the oxidized state<sup>[17]</sup> and cannot contribute to the magnetic ordering. Hence the ferromagnetic state in APhF-Co is a result solely of the alignment of  $\pi$ -electron spins on the fullerene units. Together with extensive measurements of its magnetic properties using AC susceptibility, SQUID magnetisation and electron spin resonance (ESR), we present a detailed characterisation of its electronic structure using infrared and optical measurements.

## EXPERIMENTAL

(3-nitrophenyl)-1H-1,2-methano-[60]-fullerene was obtained by reaction 3-nitrophenyldiazomethane and  $C_{60}$  in toluene solution. (3-aminophenyl)-1H-1,2-methano-[60]-fullerene (APhF) was synthesised with reduction of (3-nitrophenyl)-1H-1,2-methano-[60]-fullerene with activated iron and isolated by flash chromatography<sup>[18]</sup>. The charge transfer complex APhF-Co was synthesised by mixing a toluene solution of cobaltocene and APhF in the molar ratio of 1:1. The resulting black precipitate was washed several times with toluene to remove unreacted compounds, then with hexane and finally dried in vacuum. The structural units of the compound are shown schematically in the Figure 1.

Slow precipitation and crystallisation of the powder in the reaction of APhF with  $CoCp_2$  was found to be crucial for synthesis of FM samples. The infrared spectra and optical spectra were measured with Bomem MB 160, and HP UV-Vis spectrometers in KBr and tetrahydrofuran, respectively. ESR was measured using a Brooker ESR-300 while AC susceptibility was

measured with an ACSuS susceptometer, and the DC magnetization measurements were performed in a home-made SQUID magnetometer. All measurements were performed on powder samples kept in an inert atmosphere.

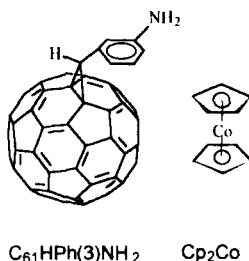


FIGURE 1 A schematic picture of the molecular building blocks in APhF-Co

## OPTICAL AND VIBRATIONAL CHARACTERIZATION

The evidence that materials synthesized from  $\text{C}_{60}$  derivatives are charge transfer complexes containing  $\text{C}_{60}$  derivatives as monoanions is: 1.) A strong room temperature ESR signal corresponding approximately to one spin per fullerene molecule 2.) strong absorption in the NIR region at about 1eV (1200 nm) corresponding to a fullerene anion transition between the HOMO and LUMO of  $\text{APhF}^-$  and 3.) characteristic vibration mode shifts in the mid-infrared vibrational spectra.

The most important evidence for full CT in solid APhF-Co comes from vibrational spectroscopy. As expected, in APhF-Co the four main fullerene-based modes are distinctly frequency shifted to 524, 572, 1191 and 1388  $\text{cm}^{-1}$ , respectively in excellent agreement with shifts in  $\text{C}_{60}^-$  anions in other doped fullerenes<sup>[19]</sup>. Careful examination of the APhF-Co spectra reveals no evidence

of the  $1427\text{ cm}^{-1}$  peak of neutral APhF, with the implication that there is no neutral APhF in the sample. The mid-infrared transmittance spectra of APhF-Co shown no evidence of any Drude absorption down to low frequencies, indicating that the material is most likely an insulator.

## MAGNETIC PROPERTIES

The low-temperature magnetic susceptibility  $\chi(T)$  magnetization  $M$  of APhF-Co measured with two different methods is shown in Figure 2.

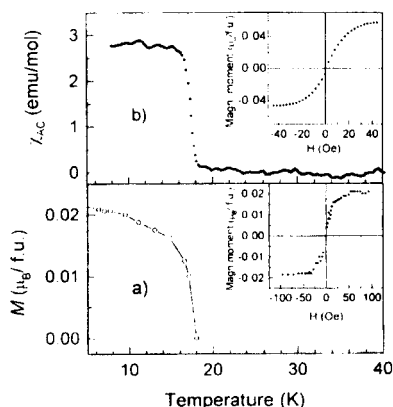


Figure 2. a) The SQUID magnetization  $M$  of APhF-Co as a function of  $T$  measured with  $H_{\text{ext}} = 30$  Oersted shows an onset at  $T = 19 \pm 0.3$  K. The magnetization curve at 4.2 K measured using the SQUID magnetometer showing full saturation at  $H = 40$  Oersted is shown in the insert. b) The AC susceptibility  $\chi_{\text{ac}}(T)$  shows a similar temperature dependence as the SQUID magnetization and the  $M$ - $H$  curve measured by the AC susceptometer at  $H = 40$  Oersted confirms the SQUID measurements with full saturation at 40 Oersted.

The DC magnetization  $M(T)$  measured with a SQUID at  $H=30$  Oersted (Fig.2a)) shows a rather characteristic rise below 18.5 K. In contrast, the AC susceptibility shows a similar abrupt increase near 19 K (Fig.2b)) and saturates rapidly, reaching a near-constant value  $\chi \approx 2.7$  emu/mol at 17 K. The magnetization curves measured directly using a SQUID magnetometer (insert to Fig. 2a)) and indirectly with an AC susceptometer and calculated from  $M(H) = \int \chi_{ac} dH$  (Fig. 2b)) both show complete saturation at  $M \cong 0.045$   $\mu_B/f.u.$  at a relatively low field of  $H=40$  Oersted (Fig.2).

The data exclude the possibility of spin-canted antiferromagnetism in this compound, since application of higher fields above 40 Oe does not increase  $M$  consistent with the suggestion that APbF-Co is a proper ferromagnet. In common with many other organic ferromagnets, APbF-Co shows no visible hysteresis within the accuracy of the measurements ( $\approx 1$  Oe.).

In the X-band ESR spectra of APbF-Co above 26 K, a *single* strong symmetric line is observed (Fig.3a)) with  $g = 2.00$ , whose intensity is consistent with one spin per formula unit, confirming the absence of spins on the donor. No other line is visible which indicates that there is no neutral  $Cp_2Co$  present<sup>[16]</sup>. The width of the line decreases monotonically from 16 Oe at 300 K, to 2 Oe at 26 K, and shows no visible anomalies at intermediate temperatures. Below  $T \cong 26$  K, an additional line appears, which grows in intensity upon reducing the temperature. The susceptibility  $\chi_0^{ESR}$  calculated from the intensity of this line is plotted as a function of  $T$  in Fig. 3b). We note that  $\chi_0^{ESR}$  shows a slight increase already at  $T=25\sim 30$ K. In addition to the increase in static susceptibility, the  $T$ -dependent ESR line also shifts and broadens at low temperature. Although the broadening is difficult to measure accurately above  $T_c$ , a lineshift is clearly evident well above  $T_c$ , at least up to



30 K, which together with the increase in  $\chi_0^{\text{ESR}}$  could be interpreted as an onset of FM above  $T_c$ .

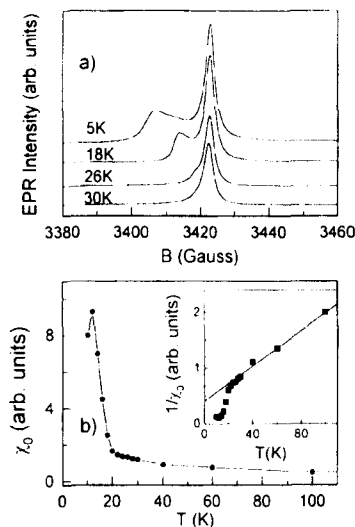


Figure 3. a) The integrated ESR intensity spectra of APHF-Co at different temperatures. Below 26 K an extra line becomes clearly visible. b)  $\chi_0^{\text{ESR}}$  from the ESR intensity starts to grow below 30 K. The insert shows a plot of  $1/\chi$  vs. T. The negative intercept is suggestive of AFM correlations at higher temperatures.

However, since no such increase in  $\chi_0$  is observed above  $T_c$  in measurements done with zero applied field, we attribute this effect to the external 3.4 kOe field of the ESR apparatus. The inverse ESR susceptibility  $\chi_0^{-1}(T)$  of the FM line, shown as a function of temperature in the insert to Figure 3b), suggests Curie-Weiss (CW) behaviour above  $T_c$  with a negative temperature intercept of  $\chi_0^{-1}(T)$  at  $T \approx 30$  K. Below 26 K,  $\chi_0^{-1}$  starts to depart significantly from the CW law, suggesting a change over from AFM to FM spin correlations.

A COMPARISON OF TDAE C<sub>60</sub> AND APhF-Co

There are some distinct and important differences in the magnetic behaviour of APhF-Co compared to TDAE-C<sub>60</sub>. First, APhF-Co shows a clear field-saturation of  $M$  below  $T_c$ , whereas TDAE-C<sub>60</sub> powder samples do not show full saturation<sup>[1,4]</sup>, secondly the susceptibility  $\chi_{AC}$  below  $T_c$  is temperature- independent in APhF-Co for  $H=0$ , while TDAE-C<sub>60</sub> shows a distinct spin-glass-like cusp at low temperatures<sup>[6]</sup> and finally in APhF-Co there is a conspicuous absence of anomalies in the ESR spectra for  $100 < T < 200$  K which are a characteristic feature in TDAE-C<sub>60</sub>. Some of these effects in TDAE-C<sub>60</sub> have been attributed to the molecular rotation of the C<sub>60</sub> molecules<sup>[6,51]</sup>, which are believed to lead to a competition between spin-glass and FM interactions at low temperatures. Their absence in APhF-Co is consistent with inhibited rotational degrees of freedom of the APhF fullerene by the adduct, possibly explaining the absence of the glass-like behaviour and absence of anomalies related to the orientational ordering at intermediate temperatures.

The saturation moment of  $\sim 0.045 \mu_B$  /f.u. in AC magnetization measurements (Fig.2b)) shows that typically only a few percent of the sample is ferromagnetically ordered. This is in agreement with X-ray analysis, which showed that the degree of crystallinity is of the same order. To emphasise the importance of the structure for achieving a FM state, we mention that Cp<sub>2</sub> Co salts of ortho and para isomers of APhF also exhibit a full CT and, judging by their vibrational, NIR and UV-Vis spectra compared to the meta isomer, show no detectable difference in electronic structure. However, repeated attempts at obtaining a FM phase with these isomers have so far proved unsuccessful, the ortho and para isomers showing antiferromagnetic ordering.

## CONCLUSIONS

To conclude, the saturation of the magnetization in both AC susceptibility and SQUID magnetization measurements together with infrared absorbance measurements enables us to classify APhF-Co as an insulating organic molecular ferromagnet whose magnetic lattice is composed of a single molecular species and has the highest Curie temperature  $T_c \cong 19$  K to date for a  $\pi$ -electron system. In contrast to TDAE-C<sub>60</sub>, we have found no spin-glass properties, but rather distinct characteristics of a proper soft ferromagnet. The antiferromagnetic nature of other cobaltocene doped isomers of APhF appears to suggest that the main problem in synthesising new organic FM compounds is in achieving the appropriate molecular crystal structure which favours FM interactions at low temperatures. The simplified magnetic structure of this compound will hopefully lead to a better understanding of the microscopic nature of the distributed  $\pi$ -electron ferromagnetic exchange interactions in fullerene materials and eventually higher  $T_c$ .

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